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TECHNICAL NOTE 2537

HEAT CAPACITY LAG IN GASES

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By Richard Walker

SUMMARY

This report reviews the literature on the sonic studies of the problem of the excitation of molecular vibrations by collision. The theory on which the interpretation of almost all the sonic work has been based is discussed rather qualitatively in some detail. The principal experimental programs are described and a table of most of the available results is included.

Of particular interest is the fact that collisions between unlike molecules are often markedly more effective in setting one of the collision partners into vibration than collisions between molecules of the same species. Attempts to explain the observed collision efficiencies both in pure and mixed gases have been only mildly successful to date. No quantitative predictions are yet possible.

Two qualitative rules appear to have considerable merit: (1) If two collision partners, of the same or different species, have a chemical affinity for each other, the probability of vibrational excitation is relatively large; (2) When the relative velocity of approach is such that the duration of the collision is of the order of the period of vibration of one of the molecules, that molecule has a large probability of being set into vibration. The first rule was suggested by Eucken; the latter, by Landau and Teller.

A good deal of the more recent work has been concerned with attempts to prove or disprove the existence of different collision efficiencies for exciting the different normal modes of vibration of molecules with more than a single mode. The experimental evidence is not very satisfying as yet.

INTRODUCTION

In the last 25 years the problem of the excitation and deexcitation of the vibrations of gas molecules by collisions has been studied in

considerable detail. The understanding of the problem as yet is largely phenomenological.

Contributions have come from four different fields of study - spectroscopy, propagation of sound, rates of chemical reactions, and aerodynamics. The major portion of the work has been done in the sonic studies. These have been largely in the ultrasonic region. Indeed, the fact that the excitation of molecular vibrations is sometimes a relatively inefficient process, several thousand collisions often being required, was first discovered experimentally in 1925 by G. W. Pierce by very accurate measurements of the velocity of sound. The phenomenon is considered to be the most important physical discovery to have come out of ultrasonics research.

The results from the four different fields of study are in apparent disagreement. In sonic work thousands of collisions are often found necessary to excite vibrations. But in the spectroscopic work, where fluorescent spectrums are studied, results indicate that almost every collision is effective in exciting vibration. Studies of the activation of unimolecular decompositions yield intermediate results. One essential difference between the conditions under which these various studies are made is the degree of vibrational excitation of the molecules. In sonic work only the lower quantum levels of vibration are excited and no electronic excitation exists. On the other hand, in fluorescence studies many vibrational quantum levels are appreciably occupied. It could be that the remarkable difficulty of exciting and dissipating molecular vibrations is characteristic only of the lower quantum levels, where the energy difference between successive levels is large. Oldenberg and Frost (1937) discuss this point of view at length in their review. Perhaps the theory of Landau and Teller (1936), which predicts a very rapid decrease in the number of collisions necessary to excite vibration with an increase in the temperature, is adequate to explain the great effectiveness of collisions in one field of experiments and not in the other.

The remarkable fact, of course, and the one with which this report is primarily concerned, is that collisions are sometimes very ineffective in exciting vibrations. The sonic experiments have exhibited this phenomenon most markedly, so the report will be confined principally to the results of those experiments. Brief mention will also be made of some recent aerodynamic studies at room temperature by Kantrowitz (1946) and Griffith (1948) in which the same phenomenon has been manifest.

Two very helpful review articles covering the results of the sonic investigations have appeared. One is the paper of Richards (1939); the other, the less well known paper by Kittel (1946).

It is the purpose of this report to review briefly the history of the important ideas prior to 1939 and to describe in more detail the work since that time, with special emphasis on the remarkable "trace catalyst" phenomenon. This phenomenon has been explained on the basis of the ability of a molecule of species B (usually added only in traces to a gas of molecular species A) to excite the vibration of an A molecule much more readily in some instances than another A molecule does.

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THEORY FOR SONIC MEASUREMENTS

Early Observations

Prior to 1925 the velocity of sound in a gas under pressure P and of density ρ was thought to be given at all frequencies by Laplace's formula

$$V = (\gamma P / \rho)^{1/2} \quad (1)$$

where γ is the ratio of the specific heat at constant pressure C_p to the specific heat at constant volume C_v . For an ideal gas, $P = RT\rho/M$, where R is the universal gas constant per mole, T , the absolute temperature, and M , the molecular weight. Equation (1) then becomes

$$V = \left[\frac{RT}{M} (1 + R/C_v) \right]^{1/2} \quad (2)$$

Other equations of state can be employed in accurate work. For example, if the boiling point of the gas is above -150°C , for velocities at room temperature the equation of state $p = (RT + Bp)\rho/M$, where B is the second virial coefficient, can be used instead. In these expressions the velocity appears to be independent of the frequency.

Absorption of sound was thought to occur from losses due solely to viscosity and heat conduction. The absorption coefficient (per cm) calculated by Stokes and Kirchhoff is of the form

$$\alpha_{cl} = \frac{2\pi^2 f^2}{V^3 \rho} \left(\frac{4}{3} \eta + \frac{\gamma - 1}{C_p} K \right) \quad (3)$$

where η is the coefficient of viscosity, K is the coefficient of thermal conductivity, V is the sonic velocity, and f is the frequency of the sound. Expression (3) represents what the writers in the field refer to as the "classical" absorption. The classical absorption is not usually appreciable until frequencies well above the audible range (above approx. 15,000) are reached. Kittel (1946) has an excellent discussion of this type of absorption and so does Bergmann (1938).

In 1925 G. W. Pierce of Harvard designed the first acoustic interferometer and found that the velocity of sound in CO_2 (carbon dioxide) increases with frequency in the ultrasonic region. Grossmann, Abello, and Pielemeier made other early velocity and absorption measurements in air and CO_2 , verified Pierce's discovery, and found that the absorption becomes almost a hundred times the classical value predicted by equation (3) in a certain region of ultrasonic frequencies.

Concept of Thermal Relaxation

The explanation for the observed dispersion of the velocity and the anomalous absorption was offered by Herzfeld and Rice (1928). They apparently borrowed an idea first suggested by Sir James Jeans in his "Dynamical Theory of Gases" (Cambridge Univ. Press, 1904). The idea is this: Thermal equilibrium between the translational (external) energy and the rotational and vibrational (internal) energies of gas molecules is not restored "instantaneously" if that equilibrium is suddenly disturbed.

For example, suppose the translational energy content of a gas is suddenly increased by "heating" the gas. Some of the added energy must be converted into rotational and vibrational energies before equilibrium, in the sense demanded by the equipartition theorem, is restored. It is hard to imagine any mechanism for effecting this energy transfer other than collisions. Now in many gases at normal temperature and pressure there are in the order of 5×10^9 collisions per molecule per second. At best one could not expect equilibrium to be restored in less time than that required for most of the molecules to have at least one collision, that is, about 0.2×10^{-9} second. But matters are not even this favorable.

Steric factors are important. A diatomic molecule cannot be set into vibration (using purely classical mechanical considerations and

assuming no net electrical charges on any of the atoms) if it is struck by another molecule moving along a line perpendicular to the line joining its two atoms. Furthermore, the internal energies are quantized. The relative translational energy of two colliding molecules, one of which is set into vibration, must be at least as large as the energy of the vibrational quantum. Very elementary considerations of this type¹ lead one to suspect that the excitation of molecular vibrations is a rather inefficient process. This conclusion is borne out by experiment. Observed adjustment times range from 10^{-8} to 10^{-2} second. These times correspond to a range of collisions from about 50 to over 10 million.

To simplify the discussion at this point another experimental result is considered. The rotational energy reaches its equilibrium value much more rapidly than the vibrational energy. Thus, in cases where the vibrational energy content of the gas is appreciable at the temperatures concerned, any phenomena which depend on the "lag" in the adjustment between external and internal energies can be adequately described by neglecting the lag of the rotational adjustment. Any observable lag is essentially that of the vibration alone.

So far, only sudden additions of energy have been considered, where the lag in establishing thermal equilibrium results from the difficulty of setting molecules into vibration. If energy is suddenly removed from the gas, the internal energy content of the gas is at first too great. It must be dissipated into heat (external energy) by collisions. Experimentally, it is found that this process, too, often requires thousands of collisions. Although the average number of collisions necessary to excite and deexcite vibrations is not the same, both these quantities can be determined experimentally.

Qualitative Explanation of Early Observations

on Basis of Thermal Relaxation

The lag in the adjustment of thermal equilibrium is often referred to as "thermal relaxation" or "heat capacity lag." Using the concept of thermal relaxation Herzfeld and Rice were able to account for the observed velocity and absorption of sound. Qualitatively, the explanation is as follows: A sound wave passing through a gas provides a mechanism for locally adding energy to, or removing energy from, the gas by virtue of alternate compressions and rarefactions. If the compressions and rarefactions occur sufficiently slowly, thermal equilibrium will be maintained throughout the acoustical cycle and one will observe a velocity given by equation (2). If, however, they occur with sufficient

¹Also, see Oldenberg (1931).

rapidity so that the time for one acoustic cycle is comparable to the time of adjustment of thermal equilibrium, the slow transfer of energy from translation to vibration keeps the internal energy from reaching its full equilibrium value. The gas exhibits an "effective" specific heat which is smaller than its full equilibrium specific heat by the extent to which the vibrational heat capacity of the gas is unable to follow the acoustical cycle. Expression (2) shows that as the effective C_v decreases the velocity increases. This is the observed behavior.

If the frequency of the sound wave becomes high enough, the total vibrational specific heat fails completely to participate in the acoustical cycle. The velocity reaches a new higher constant value given by an expression similar to equation (2) in which C_v is replaced by the specific heat of translation and rotation alone. This has also been observed experimentally.

H. O. Kneser has provided a good qualitative explanation of sound absorption arising from the thermal relaxation process. His ideas are adequately explained in Wood's (1939) book and will not be discussed here.

Mathematical Formulation

The mathematical formulation of the ideas discussed above has been made by considering the process of thermal relaxation from essentially two different points of view, as explained by Richards (1939). One is a thermodynamic, continuous fluid theory. The other is a quantized kinetic theory. The former was first developed by Einstein in 1920 when he wrote the theory for the velocity of sound in a dissociating gas. Herzfeld and Rice, Kneser, Rutgers, and Richards have all leaned heavily on the mathematical formalism developed by Einstein in their respective theoretical treatments. Bourgin fathered the quantized kinetic-theory approach. He wrote a series of papers, the last being his 1936 paper cited in the bibliography, which treated about the most general type of gas mixture imaginable. Only one other writer has followed Bourgin's method, namely, Saxton.

Simplest Possible Case

Richards (1939) presents a concise derivation of the dependence of the velocity of sound on the time of adjustment of thermal equilibrium for the simplest possible case of interest. This is the case in which the temperature is such that only the ground state and the first quantum

state of vibration are appreciably occupied. Furthermore, the molecules have only one normal mode of vibration. In general, when there are several modes present it seems reasonable to expect that certain modes are more easily excited than others. In this case there might be several independent rates of adjustment.

Fortunately, the simplest case is of wide practical interest. All the diatomic gases have only one mode of vibration. In polyatomic gases, always characterized by at least three different normal modes, often only one mode is excited appreciably at the temperature concerned. The theory for the simple case is then still applicable.

For the simplest case the gas is composed of two classes of molecules, those in the ground state of vibration (nonvibrating) and those in the first excited state (vibrating). Excitation corresponds to a transition from the ground to the first excited state ($0 \rightarrow 1$); deexcitation, to a $1 \rightarrow 0$ transition. At any instant there will be a certain number n_0 of molecules in the ground state and a number n_1 in the excited state. At all times $n_1 + n_0 = n$, the total number of molecules, a constant. The continuous exchange of molecules between states 0 and 1 is a rate process, characterized by the reaction rate equation

$$\frac{dn_1}{dt} = f_{01}n_0 - f_{10}n_1 \quad (4)$$

where f_{01} is a reaction rate constant which specifies the number of $0 \rightarrow 1$ transitions per molecule per second and f_{10} specifies the corresponding number of $1 \rightarrow 0$ transitions. At equilibrium the total numbers of transitions in each direction are equal and $dn_1/dt = 0$.

Furthermore, at equilibrium

$$n_1 = n_0 e^{-h\nu/kT}$$

so

$$f_{01} = f_{10} e^{-h\nu/kT} \quad (5)$$

where k is Boltzmann's constant and ν , which is equal to the energy associated with one vibrational quantum divided by Planck's constant h , is determined from spectroscopic data.² Most diatomic and triatomic molecules at room temperature fulfill the specifications for the simplest possible case; that is, only one normal mode of vibration is appreciably excited and that only in the first quantum state. It is then usually true that $h\nu \gg kT$ and $f_{01} \ll f_{10}$.

Using $n_0 + n_1 = n$, equation (4) becomes.

$$\frac{dn_1}{dt} = f_{01}n - (f_{01} + f_{10})n_1 \quad (6)$$

whence

$$n_1 = \text{Constant}_1 + \text{Constant}_2 e^{-(f_{01}+f_{10})t} \quad (7)$$

The number n_1 adjusts to its equilibrium value exponentially in time with the characteristic "relaxation time"

$$\beta = \frac{1}{f_{01} + f_{10}} \quad (7a)$$

Since $f_{01} \ll f_{10}$,

$$\beta \approx 1/f_{10} \quad (8)$$

Sometimes β is more appropriately called the "mean lifetime" of state 1, for it is simply related to the time a molecule exists in state 1 on the average before dropping back to the ground state. Thus β is a measure of the ease with which the molecular vibrations are deexcited. The reaction rate constant f_{01} can be found from f_{10} using equation (5) so the number of collisions necessary to excite vibration can also be determined.

²The frequency of vibration of the molecule ν should not be confused with the sonic frequency f .

The usual procedure is to multiply β , the time necessary for the departure from thermal equilibrium to be reduced to $1/e$ of its initial value, by the collision rate Z . This gives the number of collisions per molecule occurring during the time β and is referred to as the "number of collisions per molecule necessary to dissipate a vibrational quantum."

Using the general expression for the velocity of sound

$$v^2 = \left(\frac{\partial P}{\partial \rho} \right)_T + \left(\frac{\partial P}{\partial T} \right)_\rho \frac{MT}{C_p^2} \quad (9)$$

reasoning that only the specific heat C of the gas is a function of the frequency, assuming $n_0 \gg n_1$ as above, and considering the manner in which the reaction equation (4) is displaced from its equilibrium form during the passage of a sound wave, Richards (1939) derives the formula for the velocity as a function of frequency in an ideal gas which is characterized by a single adjustment process with relaxation time β . He gets

$$v = \left[\frac{RT}{M} \left(1 + R \frac{C_0 + \omega^2 \beta^2 C_\infty}{C_0^2 + \omega^2 \beta^2 C_\infty^2} \right) \right]^{1/2} \quad (10)$$

where C_0 is the total heat capacity at constant volume for the appropriate temperature, C_∞ is C_0 minus the vibrational specific heat, ω is 2π times the sonic frequency, and $\beta = 1/f_{10}$ as above. One may compare equation (10) with equation (2) to see what the effect of thermal relaxation is.

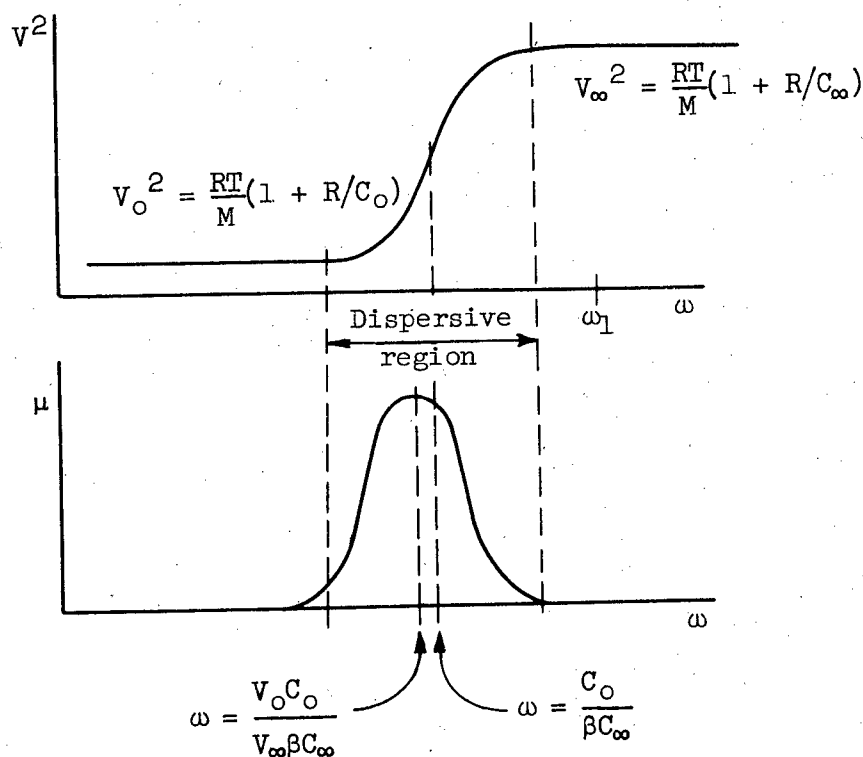
Richards also derives the expression for the absorption coefficient per wave length μ ,

$$\mu = \frac{2\pi C_\infty \omega}{C_0 f_{10}} \left[\frac{v_\infty^2 / v_0^2 - 1}{\left(v_\infty^2 / v_0^2 \right) \left(C_\infty \omega / C_0 f_{10} \right)^2 + 1} \right] \quad (11)$$

This can be written

$$\mu = 2\pi\omega f_{10} \left[\frac{R(c_0 - c_\infty)}{c_\infty(c_\infty + R)\omega^2 + c_0(c_0 + R)f_{10}^2} \right] \quad (12)$$

Expressions (10) and (12) yield the curves shown in the following figure. The velocity behaves just as anticipated in the



Velocity and absorption of sound in dispersive region, as given by equations (10) and (12).

qualitative discussion above. Note that the upper and lower terminal velocities do not depend on the relaxation time β , which measures the ease with which the molecular vibrations are excited. Only the position of the point of inflection, which occurs at $\omega = c_0/\beta c_\infty$, depends on β . The velocity curve is often referred to in the literature as the "symmetrical S-curve" for obvious reasons.

The absorption curve is a "symmetrical bell-shaped curve" which has a maximum value given by

$$\mu_{\max} = \pi \left(\frac{V_{\infty}}{V_0} - \frac{V_0}{V_{\infty}} \right) \quad (13)$$

at the frequency

$$f_{\max} = \frac{1}{2\pi} \frac{V_0 C_0}{V_{\infty} \beta C_{\infty}} \quad (14)$$

This frequency f_{\max} falls slightly below that at which the inflection point of the velocity curve occurs, but to a very good approximation the absorption is confined to the dispersive region of the velocity. Note that μ_{\max} is also independent of β . The value of β fixes only the frequency at which the maximum absorption occurs. From equation (14)

$$\beta = \frac{1}{2\pi f_{\max}} \sqrt{\frac{C_0(C_0 + R)}{C_{\infty}(C_{\infty} + R)}} \quad (15)$$

Expression (15) makes it clear why relaxation phenomena usually must be studied in the ultrasonic region. Usual values for β are around 10^{-5} or 10^{-6} second. The frequencies of the center of the dispersive region are thus of the order of 10^5 or 10^6 in many cases.

The relaxation time β increases when f_{10} decreases; f_{10} decreases when fewer $1 \rightarrow 0$ transitions are produced per molecule per second by the collisions in the gas. That is, more collisions are required to dissipate, and excite ($f_{01} \propto f_{10}$ by equation (5)), vibrations when β is large. When β is large the dispersive region is shifted to the lower frequencies. Such a shift does not affect V_0 , V_{∞} , and μ_{\max} . Thus, the dispersion occurs at relatively low frequencies

when collisions are ineffective in exciting vibrations. Anything that is done to improve the effectiveness of collisions, increasing f_{01} and f_{10} , shifts the dispersive region to higher frequencies. This observation will be useful presently in the discussion of the effect of the trace catalysts.

The absorption coefficient per centimeter α_{relax} due to thermal relaxation is related to the absorption per wave length μ by

$$\begin{aligned}\alpha_{\text{relax}} &= \mu/\lambda \\ &= \mu f/V\end{aligned}\tag{16}$$

The coefficient α_{relax} depends linearly on the sonic frequency, whereas the classical coefficient α_{cl} depends quadratically on the frequency. The total absorption of sound in the dispersive region includes the classical absorption; that is,³

$$\alpha = \alpha_{\text{cl}} + \alpha_{\text{relax}}\tag{17}$$

Near f_{max} , however, α_{cl} becomes negligible compared with α_{relax} . Above the dispersive region α_{relax} vanishes and α_{cl} becomes very appreciable.

Dependence of β on pressure.— So far little reference has been made to the collisions responsible for excitation of the vibrations. As Richards points out, an expression like equation (4) does not assume a collision mechanism at all for producing the energy transfers. It merely recognizes the fact that energy transfers do take place, with rates specified by f_{01} and f_{10} . How can one ascertain whether collisions are responsible?

First of all one recognizes that there are collisions involving only two molecules, the so-called "double collisions," those involving

³Additional absorption in the dispersive region may also occur from any other rate process present, such as chemical dissociation (see 1933 papers of Richards and Teeter in Jour. Chem. Phys.). In mixtures diffusion losses may occur (Bergmann, ch. 3). And losses accompanying translational dispersion (Primakoff, 1942) may occur in the vibrational dispersive region if the latter occurs at very high frequencies.

three molecules, the "triple collisions," and all higher-order types as well. By far the most frequent types are the double collisions.

If collisions are assumed to be responsible for the transitions, f_{10} will be proportional to the average number of collisions the molecule suffers in unit time, that is, the average collision rate in the gas. The collision rate per molecule for double collisions is proportional to ρ , the density of the gas. For triple collisions the collision rate is proportional to ρ^2 , and so forth for higher-order collisions and ρ in turn is proportional to the pressure of the gas. Consequently, if double collisions cause the energy transfers, f_{10} will be proportional to the pressure p , and β , to $1/p$.

Experimental studies have given impressive support to the collision theory of vibrational excitation. Studies of β as a function of the pressure have repeatedly indicated that double collisions are responsible in practically all gases studied to date. One case of triple collisions has been reported by Kneser (1933), but this will be discussed below in connection with the trace catalyst phenomenon.

In the event of double collisions β is proportional to $1/P$. Then V and μ as given by equations (10) and (12) become functions of f/P , where f is the sonic frequency. Most experimental curves are thus plotted with f/P or $\log f/P$ as the abscissa. Furthermore, in experimental work, once double collisions have definitely been verified by pressure studies, one can achieve the same effect by decreasing the pressure as by increasing the frequency. The ultrasonic generators used in the experimental work are either magnetostriction oscillators or quartz crystals. It is not convenient to vary the frequency continuously through the region under study using these sources, but it is a simple matter to vary the pressure continuously. Of course, continuous variations of P are feasible if triple collisions are of primary importance, too, but the fact that they are of importance must first be definitely established. Then β is proportional to $1/P^2$, of course.

Dependence of β on temperature.—The velocity of sound in the dispersive region depends in a complicated way on the temperature. In

$$V = \left[\frac{RT}{M} \left(1 + R \frac{C_0 + \omega^2 \beta^2 C_\infty}{C_0^2 + \omega^2 \beta^2 C_\infty^2} \right) \right]^{1/2} \quad (10)$$

the explicit dependence of V on $T^{1/2}$ is obvious. The heat capacity C_0 includes the vibrational specific heat, which depends on the temperature as given by the Planck-Einstein relation. And β depends on the temperature in a manner not yet thoroughly understood.

The time β is proportional to $1/f_{10}$. As pointed out above, in a collision theory of vibrational excitation f_{10} is proportional to the collision rate per molecule, which in turn is proportional to the density (or pressure) of the gas, to the gas-kinetic collision cross section, and to the mean relative velocity of the colliding molecules. The last quantity is proportional to $T^{1/2}$. But from experiment the dependence of f_{10} on the temperature is found to be much greater than just that carried by the $T^{1/2}$ factor introduced through the dependence of f_{10} on the collision rate. The theory of Landau and Teller (1936), which is also discussed at some length by Bethe and Teller (1942), predicts an added factor of $\exp T^{-1/3}$. This factor is associated with the prediction that the molecules with kinetic energies high compared with kT , that is, those in the high velocity tail of the Maxwellian velocity distribution, are the ones especially effective in exciting vibration. Kantrowitz (1946) and Bethe and Teller (1942) check the theory with experimental data like those of Eucken and Nümann (1937) and find reasonable agreement within the limit of experimental error. Typical experimental values for CO_2 and N_2O (nitrous oxide) are given in the following table.

Number of Collisions to Deexcite Vibrations
of N_2O and CO_2 as Function of Temperature
(from Eucken and Nümann, 1937)

| Temperature (°K) | Number of collisions | |
|---------------------|----------------------|---------------|
| | N_2O | CO_2 |
| 293 | 7,500 | 57,000 |
| 373 | 4,500 | 29,000 |
| 473 | 3,300 | 17,000 |
| 573 | 2,500 | 10,000 |
| 673 | 2,100 | 8,000 |

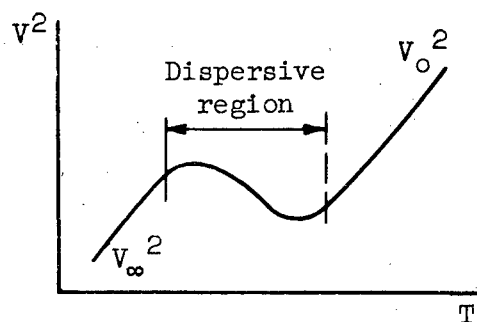
Note that the number of collisions falls off quite rapidly for these pure gases.⁴ The number of effective AB collisions in mixtures involving trace catalysts, however, seems to be rather insensitive to temperature. This is not clearly understood.

The rapid decrease in the number of collisions necessary to excite vibrations with increase of temperature may explain the observed

⁴Even these results seem to be affected by traces of impurities, for Fricke (1940) found 86,000 collisions in CO_2 at room temperature.

effectiveness of collisions in the fluorescence experiments, rather than any inherent correlation between the size of the quantum being excited and the ease with which the excitation takes place. This was mentioned in the introduction. Further experimental investigation of this matter may be needed.

It may be instructive to consider now the variation of the sonic velocity with temperature in the light of the above discussion. Imagine sound of frequency ω_1 (see fig. in section "Simplest Possible Case"), which is held constant, to be propagated through a gas whose pressure is held fixed while the temperature is varied. The initial velocity is V_∞ ; the vibrational specific heat is unable to follow the acoustical cycle. At first an increase of temperature results in an increase in the velocity. The explicit dependence on $T^{1/2}$ shown in equation (10) is the controlling factor. Further increase in the temperature increases f_{10} , because of the greater ease of vibrational excitation at higher temperatures, until the adjustment of the internal energy is able to keep pace with the rapid acoustical cycle. The velocity decreases as the effective specific heat increases, the dispersive region is traversed, and finally V_0 is reached. Then further increase of the temperature again increases V because of the explicit $T^{1/2}$ factor in equation (10). The effect of the temperature dependence of the vibrational specific heat has been neglected, as it is small. The pressure is maintained constant in order that the increase of f_{10} with an increase in pressure does not become manifest. The following figure illustrates the variation of V with T .



Isobaric variation of sonic velocity with temperature at constant acoustical frequency.

Effect of Traces of Gaseous Impurities

Richards (1934) presents the following example to illustrate the possible effect of adding a trace of a foreign gas. Consider a gas of molecular species A whose molecules are capable of vibration and in which each molecule suffers 10^{10} double collisions per second. Suppose only one AA collision in every million is effective in exciting vibration. The number of $0 \rightarrow 1$ transitions per molecule per second due to AA collisions f_{01}^{AA} is thus equal to 10^4 . Now introduce 0.1 percent of gas B, whose molecules, for the sake of simplicity, are incapable of vibration. Let B have approximately the same molecular weight and specific heat as A so that V_0 , V_∞ , and μ_{\max} are not altered appreciably. There are 10^7 AB collisions per second per A molecule. The number of $0 \rightarrow 1$ transitions per molecule per second will now include the ones occasioned by AB collisions. That is,

$$f_{01} = f_{01}^{AA} + f_{01}^{AB} \quad (18)$$

Suppose each AB collision is effective in exciting A. Then f_{01} equals $10^4 + 10^7 \approx 10^7$. The dispersive region shifts to frequencies higher by three orders of magnitude. This illustrates the "trace-catalyst effect."

If the efficiency of an AB collision is equal to or less than the efficiency of an AA collision, f_{01}^{AB} is numerically far less than f_{01}^{AA} and traces of B produce no effect. For measurements on pure gases the lowest value of f_{01} found is most likely to be correct.

Triple Collisions in Mixtures

In pure gases it is a relatively simple matter to test for possible triple collisions by studying f_{01} as a function of the pressure. In mixtures the problem is more complicated. Collisions AAA, AAB, ABB, and BBB are all possible. If B is incapable of vibration, B contributes nothing to relaxation effects and BBB collisions are of no importance. The effect of AAA collisions can be determined from studies of pure gas A. The number of collisions per A molecule per second with two B molecules is proportional to the square of the density of B gas, while the number of collisions with an A and a B is proportional to the product $\rho_A \rho_B$. Studies must be made of f_{01} as a function of the partial pressures of both A and B to determine the importance of AAB and ABB collisions. It is important that this be done at the start of

the investigation of any new mixture. Eucken and Jaacks (1935) also discuss this matter.

By observing the change in f_{01} with the partial pressure of water vapor added to oxygen (essentially), Kneser (1933) and Knudsen (1935) were able to show that triple collisions involving two water molecules were principally effective in exciting oxygen molecular vibrations.

Discrepancies

The theory of Landau and Teller (1936) introduces the following expression for β ,

$$\beta = \frac{1}{f_{10} - f_{01}} \quad (19)$$

which differs from equation (7a) by a minus sign. Expression (19) results from considering all quantum energy levels of a given mode as occupied, rather than just the 0 and 1 states.

The expression used by Knudsen and Fricke (1940) for the absorption coefficient μ , which is identical with the one also used by Knudsen and his coworkers in several earlier papers, cannot be reduced to expression (12), which was used by Richards, Eucken, and others. Knudsen writes

$$\mu = 2\pi \frac{R(C_0 - C_\infty)}{[C_0(C_0 + R)C_\infty(C_\infty + R)]^{1/2}} \frac{f_{\max} f}{f_{\max}^2 + f^2} \quad (20)$$

This probably results from the manner in which the many approximations used in the theory are introduced in the respective treatments.

More General Cases

The discussion of the simplest possible case outlines the theory on which the interpretation of practically all the acoustic experiments made to date has been based. A more general theory includes several refinements. A vibrational mode may be excited appreciably in higher

quantum levels than the first. In general, one would expect that different levels would have different lifetimes. Also, more than one mode of vibration exists in the case of all polyatomic molecules except the diatomic ones. It would seem reasonable to expect that certain modes would be easier to excite than others, as mentioned earlier. Simple geometrical considerations justify this conclusion. Finally, mixtures of two dispersive gases are of some little interest. In each of these three cases one recognizes that a multiplicity of internal energy states exists. It is no longer adequate to consider only the 0 and the 1 state of a molecule vibrating in a single normal mode. Many reaction equations of the type (4) are needed to represent the large number of adjustment processes taking place.

There are about a score of theoretical papers which treat the more complex situations mentioned above with various degrees of generality. Bourgin's work is about the most comprehensive. A large part of it had appeared by the end of 1929; the last paper, by 1936. Richards (1933) also contributed a fairly comprehensive paper. However, the above work was done prior to much of the experimental work and is not well tailored to describe the situations of most practical interest. Efforts have recently been made to strip the theory of unessential details in the light of recent evidence. Schäfer's (1940) paper represents one such treatment. Richards (1939) comments briefly about the theory applicable to the cases most likely to be encountered in experiment. The equivalence of Richards' and Schäfer's expressions for the velocity in the case of two modes with independent relaxation times is not immediately apparent, however. One of the latest papers is that of Mariens (1943).

Landau and Teller (1936) performed a calculation which predicts that all the quantum levels associated with a given mode of vibration have the same lifetimes and drop out of the vibrational specific heat at the same acoustical frequency. This justified a major simplification in the original theories of Bourgin and Richards. Schäfer has taken advantage of this simplification, as have all more recent writers. Landau and Teller's arguments are discussed by Eucken and Jaacks (1935), Richards (1939), and Kantrowitz (1946). Experimental evidence from sonic studies up to 400° C support their conclusion. However, the theory may not be comprehensive enough to include the entire range of vibrational quantum levels since the results of the fluorescence studies may disprove it in the case where the upper levels are involved. This could be due to neglect of anharmonicity in the calculations, a poor approximation at the higher levels. However, it seems quite safe to accept the theory for sonic work carried out at relatively low temperatures.

If one accepts Landau and Teller's theory, two cases remain to be considered - the problem in which several modes of vibration exist and

the problem of the mixture of two dispersive gases. The theory for the former case has been considered by Bourgin (1936), Saxton (1938), Richards (1933 and 1939), Schäfer (1940), and Mariens (1943); that for the latter case is treated somewhat briefly by Richards (1933), Richards and Reid (1934), Bourgin (1936), Schäfer (1940), and Mariens (1943). The equivalence of many of the results is difficult to establish.

The theory for the above two cases predicts the appearance of multiple dispersive regions. Qualitatively, this can be understood by the observations made below. The effects produced by the lagging vibrational heat capacity are, of course, the increase in the velocity from V_0 to V_∞ through the dispersive region and the associated abnormally high absorption. The values for V_0 and V_∞ shown in the figure in the section "Simplest Possible Case" and expression (12) for the absorption coefficient make it clear that the magnitudes of the effects produced depend largely on the size of the vibrational specific heat which is responsible for the dispersive region. Note that even vibrational heat capacities as large as R cause a change in the velocity of only a few percent. Percentagewise, the corresponding change in the absorption is much larger.

The total vibrational heat capacity of a polyatomic gas is the sum of those contributed from each of the separate normal modes of vibration. For example, in CO_2 at 28°C the vibrational heat capacity of the deformation mode is about 1.82 calories per mole per $^\circ\text{C}$; that due to the symmetrical valence mode, 0.161; and that of the unsymmetrical valence mode, 0.0034.⁵ The total vibrational heat capacity is thus about 1.98 calories per mole per $^\circ\text{C}$. The dispersive effects produced by the contribution from the deformation mode will far outweigh those produced by the symmetrical valence mode, and the unsymmetrical mode will completely escape detection at this temperature; practically, then, one only needs to consider the effects of the first two. This is the reason several theoretical papers treat gases in which only two modes of vibration occur, although actually, of course, all polyatomic except diatomic molecules have at least three normal modes of vibration.

Suppose the valence mode in CO_2 were much easier to excite, that is, did not require so many collisions as the deformation mode. The valence contribution to the vibrational heat capacity would be able to maintain thermal equilibrium with the external energy of the gas at higher acoustical frequencies than the deformation mode. One would find a dispersive region at relatively low frequencies caused by the failure

⁵From Pielemeier, Saxton, and Telfair (1940).

of the deformation heat capacity to follow the acoustical cycle and a region at higher frequencies caused by the valence heat capacity. The change in velocity produced by the former would be much larger than that produced by the latter. Of course, the two dispersive regions might overlap, making the detection of the valence region more difficult.

In a mixture of two gases the total specific heat of the mixture is given by

$$C = (1 - h)C_A + hC_B \quad (21)$$

where the specific heats are per mole and h is the molar concentration of gas B. The expression for the vibrational part is of similar form if both gases are polyatomic. Consider a mixture of two polyatomic gases A and B. If the combined effect of AA and AB collisions is to excite A vibrations much more easily than BA and BB collisions excite B, the part of the vibrational heat capacity due to B will drop out at lower frequencies than the heat capacity of A. The magnitude of the dispersive effects produced by B will depend on h . If B is added only in traces, the dispersive region produced by B will escape experimental detection, and the theory for the simplest case can be applied if A meets the required specifications. This is the reason the catalytic effect of B on A molecules has been investigated by adding only traces of gas B.

The problem of determining whether certain modes of vibration are easier to excite than other modes is very interesting. But little progress has been made so far. It is practically limited to the study of relatively few molecules. For, before information can be gained about the characteristics of the modes which determine their respective ease of excitation, two things must be known - the normal modes of vibration of the molecule under study, and the frequencies of those modes. The latter are needed to calculate the vibrational heat capacity in order that the sonic measurements may be properly interpreted. These frequencies are known for only a small number of polyatomic molecules.

The history of the experimental studies from their beginning until about 1940 was marked by repeated failures to detect more than one dispersive region. It had seldom been doubted by any of the investigators that, inherently, different modes must be excited with different efficiencies. Bethe and Teller (1942) and others offered the following argument to explain the unexpected experimental observations: Once the mode most easily excited directly by the transfer of translational energy is set into vibration, the other modes will be excited from the

first through the coupling provided by the anharmonic interatomic forces, and this will occur very rapidly, within the time needed for only a few collisions.

However, experimental evidence for the existence of multiple dispersive regions began to appear shortly after 1940. The observed effects are small and the evidence is not yet comfortably convincing. Pielemeier (1943) summarizes the case for CO_2 , in which indications point to the existence of two separate relaxation times. Pielemeier's interpretation of experimental results is based on Saxton's (1936) paper on absorption theory. Alexander and Lambert (1942) report three dispersive regions in acetaldehyde (CH_3CHO); but Jatkar and Lakshiminarayanan (1946) claim the lowest region is due to an apparatus effect that was not corrected for. They also discuss evidence for two dispersive regions in CO_2 , CS_2 (carbon disulfide), and N_2O .

Buschmann and Schafer (1941) report some accurate velocity measurements on CO_2 , N_2O , NH_3 (ammonia), and $(\text{CH}_3)_2\text{O}$ (methyl ether), in which they study the possibilities for multiple dispersion.⁶ They interpret their results in terms of Schafer's (1940) theory. Schafer had shown that the typical S-shaped dispersion curve resulting when only a single mode is present is only slightly altered by a second mode which contributes a relatively small share to the vibrational heat capacity and which possesses a different relaxation time. He treated two cases of possible interest. In the first, the two modes are excited independently by direct transfer of translational energy; in the second, one mode is excited directly by translation and the other mode is set into vibration through its coupling with the first. The latter case is essentially the mechanism suggested by Bethe and Teller, except the excitation of the coupled mode need not take place during the time needed for only a few collisions in Schäfer's formulation. In their experimental study Buschmann and Schäfer conclude that the mechanism of independent excitation of the two modes occurs in CO_2 . For N_2O and NH_3 they are unable to conclude which mechanism occurs. And for methyl ether the application of Schäfer's theory is not justifiable because of the large number of modes excited in such a complex molecule.

In complex molecules like acetaldehyde it is not surprising to find multiple dispersive regions quite easily. Several modes of vibration must be appreciably excited at room temperature. It would be interesting to investigate other complex molecules to see just what multiplicity of dispersive regions can be found. But the modes excited and the corresponding frequencies of vibration are unknown for the most

⁶The author has only seen the account of this work in Chemical Abstracts, vol. 37, 1943, p. 2635.

part. Thus little information about the characteristics of the modes which determine their respective ease of excitation can be gained in such studies.

On the other hand, for simple molecules like CO_2 , whose modes and vibrational frequencies are well-known, almost invariably only one of the modes is excited to any appreciable extent at room temperature. This mode always seriously masks the dispersive effects produced by the others. The obvious solution to this difficulty seems to be to increase the temperature. After Pielemeier, Saxton, and Telfair (1940) had studied CO_2 at 28°C and found a faint suggestion of a different dispersive region due to the valence mode, Pielemeier and Byers (1943) made further studies at 98°C . This improves the situation on two counts. First, the contribution of the valence vibration to the heat capacity increases. Second, the ratio of the deformation heat capacity to the valence heat capacity decreases, cutting down the masking effect of the deformation mode. The contributions to the vibrational specific heat of CO_2 at 98°C are 2.237, 0.302, and 0.016 calories per mole per $^\circ\text{C}$ for the deformation, symmetrical valence, and unsymmetrical valence modes, respectively. Pielemeier and Byers obtained some rather disappointing results. For increasing the temperature increased the respective f_{10} 's associated with the deformation and valence adjustments at different rates, in such a way as to cause the dispersive regions nearly to merge. This behavior may be just coincidental in CO_2 . It may be possible to find gases in which the effect of increasing the temperature is to separate the two regions.

EXPERIMENTAL RESULTS

Concerning Techniques

No effort will be made in this report to describe the various experimental techniques available. Richards (1939), Hubbard (1940), and Kittel (1946) have adequate descriptions of the sonic methods. Kittel lists several of the pertinent later papers.

Only the Kantrowitz (1946) gas-dynamics technique of measuring relaxation times was unknown to the above writers. The method has one principal advantage in that measurements of relaxation times can be made over an exceedingly wide range of values by properly adjusting the dimensions of the elements of the apparatus. Kantrowitz (1947) was able to measure both the relaxation times of nitrogen, of the order of 10^{-2} second, and of hydrogen H_2 (rotational), of the order of 10^{-8} second.

A principal disadvantage of the method is the large quantity of gas

required. In view of the great experimental difficulties occasioned by the trace catalytic effect, necessitating elaborate purification techniques, this is a decided drawback.

Griffith (1949) checked Kantrowitz's original theoretical results by looking at the problem from a somewhat different point of view. He also subjected the problem of the gas flow about the impact tube to a critical examination and showed what pressure head defects could be expected from a flat-ended impact tube in comparison with those from Kantrowitz's "source-shaped" tube (see Kantrowitz's 1946 description of his measurement technique). Finally, Griffith studied several interesting pure gases for the first time, but it is unfortunate that the technique did not warrant more care in purifying the gases used. Some of his results are listed in table I but it is possible they may be influenced by traces of gaseous impurities.

So far the theory for Kantrowitz's measurement technique has only been developed for the simplest possible case.

Principal Experimental Programs

Aside from the work of Kantrowitz and Griffith, all the work reported here was done employing one of the sonic techniques. The chief contributors have been Eucken, Richards, Kneser, Knudsen, Pielemeier, Van Itterbeek, and their collaborators. Each of their programs is outlined briefly below.

Eucken: One of the first papers written by Eucken and his coworkers was that of Franck and Eucken (1933). They were aware of the early work by Pierce in CO_2 , the studies of Kneser on CO_2 and N_2O , and the work reported by Richards and Reid on CO_2 , CS_2 (carbon disulfide), SO_2 (sulfur dioxide), and C_2H_4 (ethylene). Richards and Reid had discovered the remarkably enhanced ability of H_2 to excite C_2H_4 and the ineffectiveness of argon and nitrogen in exciting C_2H_4 . Eucken, Mucke, and Becker had worked with N_2 (nitrogen), O_2 (oxygen), and Cl_2 (chlorine). The early attempts by Oldenberg, Heil, Zener, and Rice to explain the experimental results were known. And the excitation of molecular vibrations by electrons with good yield had been found by Harries and Ramien.⁷ The results of the latter studies were one of the first indications that purely classical mass considerations were not adequate to solve the transfer of energy problem.

⁷For the references to these studies see the paper of Franck and Eucken, 1933.

The early work led Eucken and Franck to think in terms of the mutual disturbance of the potential energy curves of two collision partners as playing a large role in determining the probability of vibrational energy transfer. On the basis of this idea, Eucken and Becker (1933) undertook the investigation of Cl_2 and CO_2 . Chlorine was chosen because it possesses only one mode of vibration and is therefore easiest to deal with theoretically; only its lowest quantum state is appreciably excited at room temperature. Carbon dioxide was selected to see if there is a basic difference in the ease with which the valence vibration, as in Cl_2 , and the deformation vibration are excited. A number of foreign gases were added to Cl_2 and CO_2 , constituting one of the first important studies of the trace catalyst effect. Several foreign molecules were found to be especially effective in exciting Cl_2 and CO_2 .

Eucken and Becker (1934) examined the experimental technique for measuring sonic velocities and the interpretation of experimental data very critically and then added to the data on Cl_2 and CO_2 , studying the temperature dependence of the collision yield. It was in this study that one of the most important ideas ever suggested to explain the effect of the trace catalysts was put forth. As an outgrowth of the thought in terms of potential-energy curves it was noted that the ability of a B-type molecule to excite an A seemed to be largely enhanced if A and B had a strong chemical affinity for each other. Helium appeared to be an exception.

In order to test the chemical-affinity idea further, Eucken and Jaacks (1935) studied the trace-catalyst phenomenon in N_2O , which was chosen because its physical properties were very similar to those of CO_2 , but its chemical properties were importantly different. The results of this investigation supported the chemical-affinity idea quite well.

Eucken and Nümann (1937) made further improvements in the measurement technique in order to make studies up to 400°C in CO_2 and N_2O . It was hoped that a second dispersive region, due to the valence mode, might appear. But within the limits of experimental error only one was found. With variation of the temperature a comparatively small change in effective AB collisions was discovered.

Eucken and Küchler (1938) reviewed the previous work of Eucken and collaborators and tried to explain the insensitive temperature dependence of effective AB collisions on the basis of potential-energy-curve arguments, but these are not very satisfying. Küchler (1938) made temperature studies in $\text{CO}_2\text{-He}$ (helium), $\text{CO}_2\text{-H}_2$, and $\text{N}_2\text{O-He}$ mixtures and found behavior similar to that in the earlier temperature work in mixtures.

Eucken and Aybar (1940) tested the idea that resonance coupling between the different modes of vibration of a molecule is responsible for the appearance of only one dispersive region by making measurements on pure CH_4 (methane) and COS (carbonyl sulfide), in which no simple resonances exist between the different normal modes. Still no multiplicity of dispersive regions appeared.

Schäfer (1940) then performed the calculations discussed previously and computed a possible second relaxation time in CH_4 and COS from the data of Eucken and Aybar. Finally, Buschmann and Schäfer (1941) studied the possibility of multiple dispersion in CO_2 , N_2O , NH_3 , and methyl ether.

Richards: After an early theoretical study by Richards (1933), Richards and Reid (1934) investigated CO_2 , CS_2 , and SO_2 . They used the Van der Waals equation of state to predict the velocity. Because of the agreement between the predicted and measured values of V they concluded that the adjustment of the Van der Waals forces is able to keep pace with the acoustical cycle at frequencies up to 451 kilocycles and pressures as low as 70 millimeters of mercury. They verified the double-collision hypothesis in these gases and were surprised to find the adjustment to thermal equilibrium is made three times more easily in CS_2 than in CO_2 . The two gases resemble each other so closely in physical structure.

In another investigation Richards and Reid (1934) studied C_2H_4 , pure and in mixtures with argon, helium, nitrogen, and hydrogen. The first three added gases, they concluded, have no appreciable effect in exciting ethylene vibrations, but hydrogen is very effective.

Richards (1936) concluded his experimental work on the problem by testing Eucken's chemical-affinity idea. He added hydrogen H_2 and deuterium D_2 to ethylene C_2H_4 separately. Each presumably has the same chemical affinity for ethylene. Surprisingly, he found that hydrogen is 10 times, deuterium, only 1.25 times, as effective as ethylene itself in exciting the vibrations of ethylene. He suggested two alternative explanations: (1) The uniquely small moment of inertia of hydrogen results in very large rotational quanta. Perhaps these approximately "match," or are in resonance with, some vibrational quantum of C_2H_4 , facilitating easy transfer of vibrational energy to the ethylene. (2) The short duration of a H_2 - C_2H_4 collision compared with that of a D_2 - C_2H_4 collision might account for the difference. "An instantaneous blow on one of the hydrogens in ethylene would provoke severe distortional vibration of the molecule, whereas if it were struck

sufficiently slowly the result would be merely to make the molecule rotate as a whole." This is essentially the idea which Landau and Teller (1936) have also proposed.

Kneser: Like Richards, Kneser has divided his attention between theory and experiment. One of his early papers (1933) was a highly successful explanation of some of the first observations, those of Knudsen in air and oxygen, on the basis of the new relaxation theory. He added to the evidence for Eucken's chemical-affinity hypothesis in his experimental studies (1934 and 1935) of O_2 containing foreign gases. He reviewed the experimental studies in his 1938 paper and reviewed some of the theory in 1943.

Knudsen: Knudsen is probably best known for his discovery of the trace catalyst phenomenon in early experimental studies of sound absorption in air as a function of relative humidity. Kneser helped interpret his observations. Knudsen wrote a summary of his early work in 1936. In collaboration with Fricke and Obert he made other interesting catalyst studies in 1936 and 1940.

Pielemeier: In addition to early work concerned with experimental techniques, Pielemeier, in conjunction with Saxton and Telfair (1940), made an important study of the CO_2 - H_2O mixture problem. Pielemeier (1943) also summarized the multiple dispersion effects in CO_2 , as mentioned earlier.

Van Itterbeek: Much of the best work on mixtures has been done by Van Itterbeek and coworkers, who have employed painstaking purification techniques to assemble a vast amount of important data.

Most of the results of these investigators are shown in table I. An enormous difference exists between the values obtained from laboratory to laboratory. This is largely due, no doubt, to the strong influence certain trace impurities exert. No attempt has been made to make any selective evaluation of the data. With the exception of a few gases for which the author has been unable to find sufficient collision rate information, most of the known results have been tabulated.

In comparing the effects of various foreign molecules on a given A-type molecule, it is perhaps more significant to confine one's attention to the results of one investigator at a time. For example, Knudsen and Fricke (1940) and Van Itterbeek, De Bruyn, and Mariens (1939) would agree that H_2O (water) is significantly more effective than H_2 in exciting CO_2 vibrations. Yet if one were to compare the results on H_2 of the former investigators with the results on H_2O of the latter,

it would appear that H_2 and H_2O were about equally effective. Knudsen and Fricke (1940) report values that are consistently smaller than those of others for mixtures.

For Griffith's results on complex molecules like methyl chloride and butadiene (latter not listed in table) it is possible that the relaxation times he reports cannot be simply interpreted. He has calculated them on the basis of the theory for the simplest possible case, the only case for which the theory of the Kantrowitz measurement technique has been developed. In view of the recent evidence for the existence of multiple dispersive regions in complex molecules like acetaldehyde, such a calculation may not be justified. The development of the theory for more general cases here would clarify the situation.

INTERPRETATION OF RESULTS

Because of the wide difference in the values reported for any specific case and because of the inherent complexity of the problem, it is hard to do much but make a few broad general statements about the experimental observations. Practically no quantitative predictions are yet possible.

Pure Gases

In the case of pure gases, more collisions seem to be required the higher the vibrational frequency of the molecule. Kittel (1946) points out the correspondence of the vibrational frequencies of CO_2 , N_2O , COS , and CS_2 with their observed ease of excitation. Griffith (1949) finds a similar correspondence for the observed relaxation times of CH_4 , CH_3Cl (methyl chloride), and CHF_2Cl (chlorodifluoro-methane). And Bethe and Teller (1942) feel that the large number of collisions necessary to excite O_2 is probably due to its high vibration frequency. Griffith (1949) reported very short relaxation times in complicated molecules like propane, butane, butadiene, and propylene. Such molecules must always possess certain appreciably excited low-frequency modes at room temperature. One significant exception in Griffith's results appears to be ethylene oxide, $(CH_2)_2O$, which has a surprisingly large relaxation time. (Many of Griffith's results have been omitted from table I for lack of sufficient collision rate data.)

Added Foreign Gases

The situation in the case of the trace-catalyst effect is not quite so clear. Probably the two most important influences are (1) the chemical affinity of the collision partners and (2) B-type molecules with very high average velocities, like H_2 and He. Other factors which have been suggested as being of possible importance are electric dipole moment (Metter, 1937 and 1939) and the moment of inertia of B (Richards, 1936).

The theory of Landau and Teller (1936) predicts that aside from chemical-affinity effects one other criterion can be applied. This is the ratio of the average duration of a collision to the natural period of the degree of freedom being excited. If this ratio is much larger than unity, many collisions will be required to set molecule A into vibration. It should be interesting to test this idea by experiments in which gases a and b, both capable of vibration, are alternately used as the basic gas A and the trace gas B. If chemical affinity is the controlling factor, their effects on each other in the two experiments should be mutually important. However, using Landau and Teller's criterion, their effects on each other might be importantly different.

Some attempts have been made to account for the experimental results on the basis of quantum theory studies of energy transfer during collision. A number of papers which describe this work are listed in a separate section of the bibliography, but they have not been too successful to date. The best results appear to have been achieved by Castellan and Hulburt (1950) whose theoretical predictions favorably compared with several of Eucken's experimental results.

RELATED STUDIES

When the sonic frequency is high enough so that the wave length is of the order of the mean free path in the gas, an additional dispersive region is introduced. The velocity decreases with the frequency here. The phenomenon is called translational dispersion and is discussed by Primakoff (1942).

Van Isterbeek and Thys (1938) discovered the dependence of the relaxation time in O_2 on magnetic field strength, but no theoretical explanation has yet been offered.

Rotational dispersion in H_2 has been found by Ellen Stewart (1946). Rhodes (1946) discusses the theory. The theory for the simplest case is

not valid here. Evidence points to the inadequacy of considering double collisions only in H_2 .

Several other interesting related studies are listed in the miscellaneous section of the bibliography.

Iowa State College
Ames, Iowa, June 10, 1950

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TABLE I

AVERAGE NUMBER OF COLLISIONS WITH B-TYPE MOLECULES NECESSARY
TO DEACTIVATE VIBRATING A MOLECULE AT 293° K

| Molecule | | Investigator | Collisions |
|------------------|----------------------------------|---|----------------------|
| A | B | | |
| Cl ₂ | Cl ₂ | Eucken and Becker (1934) | 34,000 |
| Cl ₂ | Ar | Eucken and Küchler (1938) | >34,000 |
| Cl ₂ | He | Eucken and Becker (1934) | 900 |
| Cl ₂ | H ₂ | -----do----- | 780 |
| Cl ₂ | N ₂ | -----do----- | >34,000 |
| Cl ₂ | CO | -----do----- | 230 |
| Cl ₂ | HCl | -----do----- | 120 |
| Cl ₂ | CH ₄ | -----do----- | 190 |
| O ₂ | O ₂ | Kneser (1935) | >500,000 |
| O ₂ | He | -----do----- | ^a 150,000 |
| O ₂ | H ₂ | -----do----- | 20,000 |
| O ₂ | N ₂ | -----do----- | ^a 100,000 |
| O ₂ | CO | -----do----- | ^a 8,500 |
| O ₂ | O ₃ | -----do----- | ^a 33,000 |
| O ₂ | CO ₂ | -----do----- | ^a 25,000 |
| O ₂ | H ₂ O | -----do----- | 400 |
| O ₂ | H ₂ S | -----do----- | 4,200 |
| O ₂ | NH ₃ | -----do----- | 390 |
| O ₂ | C ₂ H ₂ | -----do----- | 1,200 |
| O ₂ | CCl ₄ | -----do----- | ^a 4,200 |
| O ₂ | HCCl ₃ | -----do----- | ^a 8,500? |
| O ₂ | C ₂ H ₅ OH | -----do----- | 120 |
| O ₂ | C ₆ H ₆ | -----do----- | 400 |
| CO | CO | Sherratt and Griffiths (1934) | 60,000 |
| H ₂ O | H ₂ O | Kantrowitz (1947) | ^b 400 |
| CO ₂ | CO ₂ | Eucken and Aybar (1940) | 50,000 |
| | | Eucken and Nümann (1937) | 57,000 |
| | | Eucken and Becker (1934) | 51,000 |
| | | Fricke (1940) | 86,000 |
| | | Van Itterbeek, De Bruyn, and Mariens (1939) | 120,000 |
| | | Van Itterbeek and Mariens (1938) | 90,000 |
| CO ₂ | He | Küchler (1938) | 2,600 |
| CO ₂ | Ne | Eucken and Becker (1934) | 1,700 |
| CO ₂ | Ar | Eucken and Becker (1933) | >50,000 |
| CO ₂ | H ₂ | Eucken and Becker (1933) | >50,000 |
| | | Eucken and Küchler (1938) | 47,000 |
| | | Küchler (1938) | 300 |
| | | Eucken and Becker (1934) | 480 |
| | | Knudsen and Fricke (1940) | 215 |
| | | Van Itterbeek, De Bruyn, and Mariens (1939) | 560 |
| CO ₂ | D ₂ | -----do----- | 1,700 |
| CO ₂ | O ₂ | -----do----- | >100,000 |
| CO ₂ | CO | Eucken and Aybar (1940) | 6,200 |
| CO ₂ | HCl | Eucken and Becker (1934) | 130 |
| CO ₂ | H ₂ O | Küchler (1938) | 105 |
| | | Eucken and Becker (1934) | 34 |
| | | Knudsen and Fricke (1940) | 17 |
| CO ₂ | D ₂ O | Van Itterbeek, De Bruyn, and Mariens (1939) | 150 |
| | | Van Itterbeek, De Bruyn, and Mariens (1939) | 300 |

^aApproximate value.^bTemperature T = 485° K.





TABLE I

AVERAGE NUMBER OF COLLISIONS WITH B-TYPE MOLECULES NECESSARY
TO DEACTIVATE VIBRATING A MOLECULES AT 293° K - Concluded

| Molecule | | Investigator | Collisions |
|--------------------|---|---------------------------|--------------------|
| A | B | | |
| CO ₂ | CH ₄ | Eucken and Becker (1934) | 2,400 |
| CO ₂ | CH ₃ OH | Knudsen and Fricke (1940) | 36 |
| CO ₂ | C ₃ H ₇ OH | -----do----- | 25 |
| CO ₂ | C ₆ H ₅ CH ₃ | -----do----- | 25 |
| | (toluene) | | |
| CO ₂ | H ₂ S | -----do----- | 1,200 |
| N ₂ O | N ₂ O | Küchler (1938) | 7,500 |
| | | Eucken and Jaacks (1935) | 5,500 |
| | | Fricke (1940) | 11,800 |
| | | Küchler (1938) | 1,000 |
| N ₂ O | He | Eucken and Nümann (1937) | 1,400 |
| | | Eucken and Jaacks (1935) | 1,600 |
| | | Eucken and Küchler (1938) | 33,000 |
| N ₂ O | Ar | Eucken and Jaacks (1935) | 650 |
| N ₂ O | H ₂ | Knudsen and Fricke (1940) | 110 |
| | | Eucken and Jaacks (1935) | 440 |
| N ₂ O | D ₂ | -----do----- | 3,600 |
| N ₂ O | CO | -----do----- | 60 or 70 |
| N ₂ O | H ₂ O | Küchler (1938) | 105 |
| | | Knudsen and Fricke (1940) | 57 |
| | | Eucken and Jaacks (1935) | 450 |
| N ₂ O | NH ₃ | Eucken and Jaacks (1935) | 840 |
| N ₂ O | CH ₄ | Knudsen and Fricke (1940) | 95 |
| N ₂ O | CH ₃ OH | -----do----- | 50 |
| N ₂ O | C ₃ H ₇ OH | -----do----- | 200 |
| N ₂ O | C ₆ H ₅ CH ₃ | | |
| COS | COS | Eucken and Aybar (1940) | 17,700 |
| | | Fricke (1940) | 9,600 |
| COS | He | Eucken and Aybar (1940) | 1,250 |
| COS | Ar | -----do----- | 7,750 |
| COS | H ₂ | -----do----- | 200 |
| | | Knudsen and Fricke (1940) | 130 |
| COS | N ₂ | Eucken and Aybar (1940) | 3,550 |
| COS | O ₂ | -----do----- | 3,200 |
| COS | CO | -----do----- | 2,000 |
| COS | H ₂ O | Knudsen and Fricke (1940) | 8 |
| COS | CH ₃ OH | -----do----- | 37 |
| COS | C ₃ H ₇ OH | -----do----- | 24 |
| CS ₂ | CS ₂ | Fricke (1940) | 8,700 |
| CS ₂ | H ₂ | Knudsen and Fricke (1940) | 220 |
| CS ₂ | H ₂ O | -----do----- | 18 |
| CS ₂ | CH ₃ OH | -----do----- | 83 |
| CS ₂ | C ₃ H ₇ OH | -----do----- | 48 |
| CS ₂ | C ₆ H ₅ CH ₃ | -----do----- | 200 |
| SO ₂ | SO ₂ | Fricke (1940) | 1,900 |
| | | Griffith (1949) | 2,700 |
| | | Griffith (1949) | 1,170 |
| NH ₃ | NH ₃ | Byers (1943) | ^a 5,000 |
| CF ₄ | CF ₄ | Griffith (1949) | ^a 200 |
| CH ₄ | CH ₄ | Eucken and Aybar (1940) | ^c 4,400 |
| CH ₄ | H ₂ | -----do----- | ^c 2,700 |
| CH ₄ | CO ₂ | -----do----- | ^c 460 |
| CH ₃ Cl | CH ₃ Cl | Griffith (1949) | 1,850 |

^aApproximate value.^cTemperature T = 382° K.

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| <p>NACA TN 2537 National Advisory Committee for Aeronautics. HEAT CAPACITY LAG IN GASES. Richard Walker, Iowa State College. November 1951. 40p. diagrs., tab. (NACA TN 2537)</p> <p>A review is presented of the literature on the sonic studies of the problem of the excitation of molecular vibrations by collision and the theory on which the interpretation of almost all the sonic work has been based is discussed. The principal experimental programs are described and most of the available results are included in a table.</p> <p>Copies obtainable from NACA, Washington</p> | <p>1. Aerodynamics, Fundamental (1.1) 2. Summaries, Technical (12) I. Walker, Richard II. NACA TN 2537 III. Iowa State Coll.</p>  | <p>NACA TN 2537 National Advisory Committee for Aeronautics. HEAT CAPACITY LAG IN GASES. Richard Walker, Iowa State College. November 1951. 40p. diagrs., tab. (NACA TN 2537)</p> <p>A review is presented of the literature on the sonic studies of the problem of the excitation of molecular vibrations by collision and the theory on which the interpretation of almost all the sonic work has been based is discussed. The principal experimental programs are described and most of the available results are included in a table.</p> <p>Copies obtainable from NACA, Washington</p> | <p>1. Aerodynamics, Fundamental (1.1) 2. Summaries, Technical (12) I. Walker, Richard II. NACA TN 2537 III. Iowa State Coll.</p>  |
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